



Thermoresponsive Wettability of Photonic Crystals Fabricated by Core–Shell Poly(styrene-acrylamide) Nano/Microspheres

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The photonic crystals (PCs) films with tunable wettability were fabricated from self-assembly of an amphiphilic latex nano/microspheres poly(styrene-acrylamide) at different temperatures. The results demonstrate that the surface wettability of the PCs film can be tuned from high hydrophilic (CA, 17°) to high hydrophobic (CA, 127.8°) by controlling the assembly temperature from 30 °C to 90 °C, while the position of the photonic stopbands of the PCs films unchanged virtually. The obvious wettability transition is due to the change of the surface chemical component of the latex spheres, which mainly derives from the phase separation of polymer segments driven toward minimum interfacial energy. The facile method could open new application fields of PCs in diverse environments.

Keywords: Wettability, Photonic Crystals, Core–Shell Poly(styrene-acrylamide), Nano/Microspheres.

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1. INTRODUCTION

The photonic crystals (PCs) with special properties, derived from a periodic arrangement of different dielectric materials, have been paid much attention due to their promising applications in smart windows, chemical sensors, optical devices, and memory devices.^{1–19} Particularly, the surface wettability of PCs film is an important parameter and decides its possible application in the solution system. For example, the suitable wettability favors full wetting and spreading of the precursor to infiltrate into the PCs structure⁹ and swift diffusion of the detected materials into the PCs film for the highly sensitive sensors^{10–12} or highly efficient catalyzers.¹³ Furthermore, the colloidal PCs with special wettability can also provide self-cleaning properties for optical devices.^{1,9}

Generally, the wettability of a solid surface is governed by the chemical composition and the geometric microstructure. Rough surface can effectively amplify both the hydrophobicity of the hydrophobic surface and the hydrophilicity of the hydrophilic surface.^{21–24} To PCs, three-dimensional opal or inverse opal PCs fabricated from the colloidal latex nano/microspheres, provide the intrinsic rough surface derived from colloidal crystals, which could improve the surface wettability of the films

remarkably.^{8–17,20} Gu and co-workers^{9,14} reported pioneering work by successfully utilizing the intrinsic rough surface of titanium dioxide inverse opal PCs to create superhydrophobic or superhydrophilic films. However, in their work, traditional, expensive, low-energy materials of fluorides or silanes were used. Song's group^{15–17} has self-assembled the amphiphilic core-shell particles, Poly(styrene-*n*-butyl acrylate-acrylic acid) or Poly(styrene-methyl methacrylate-acrylic acid), into colloidal crystal films and realized the wettability transition from superhydrophilic to be superhydrophobic of the films by controlling the composition of the latex sphere, assembly temperature or pH. Recently, Mangeney and co-workers²⁰ reported a new type of colloidal crystal films from thermoresponsive core-shell particles of Poly(styrene/ α -tert-butoxy- ω -vinylbenzylpolyglycidol) and created the reversible wettability transition from hydrophilic to hydrophobic by tuning the assembly temperature. These amphiphilic particles may open a new and potentially general way of controlling the wettability of PCs film by adjusting the assembly temperature. However, its application might be restricted, owing to the complex fabrication procedure of nano/microspheres and specific high transition temperature. Therefore, fine control of the wettability transition of PCs films at a desired temperature is of great importance for its practical utilization at the different temperatures.

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In this work, the wettability transition of PCs films can be easily controlled by assembly temperature without special procedure or apparatus, using monodisperse amphiphilic core–shell poly(styrene-acrylamide) (noted as P(St-AAm)) nano/microsphere with a hard polystyrene (PS) core and a soft polyacrylamide (PAAm) shell, which was synthesized by a simple one-step emulsion polymerization method. The wettability of the film could be tuned from high hydrophilic (water contact angle (CA) is 17°) to be high hydrophobic (water CA is 127.8°) by varying the assembly temperature, while the position of the stopband of the PCs films unchanged virtually. This method of fabricating PCs films with tunable wettability and invariable stopband by simply changing the assembly temperature would open new application fields of PCs in diverse environments.

2. EXPERIMENTAL DETAILS

2.1. Materials

Styrene (St) (from Sigma) was distilled under reduced pressure before using. Acrylamide (AAm) (from Fluka) was purified by recrystallization from water. Ammonium persulfate (APS) (from Tianjin Chemicals Co.) was recrystallized from water and dried under vacuum. Other reagents were analytical grade or better and used without further purification.

2.2. Synthesis of Monodisperse Core–Shell P(St-AAm) Nano/Microsphere

P(St-AAm) nano/microsphere was prepared via emulsion polymerization.^{25–28} Briefly, St (20 g), Sodium Oleat (0.003 g), NaHCO_3 (0.2 g), and NaCl (0.02 g) were dispersed in 100 g water and stirred at 300 rpm for 30 min. Then AAm (1.0 g) was added to the mixture and bubbled with nitrogen for 30 min at room temperature. The reaction mixture was kept at 60°C for 0.5 h. Following the addition of APS (0.7 g), the polymerization was carried out at 80°C for 8 h with continuously stirring. The resulting latex spheres were used directly without purification. The polydispersity of the latex spheres was about 0.005.

2.3. Fabrication of Photonic Crystals Films

The P(St-AAm) PCs films were fabricated on glass substrates by vertical deposition method.²⁵ Glass slides were, firstly, treated with a chromic-sulfuric acid solution to ensure clean surfaces and were vertically positioned in a vial containing the nano/monodisperse P(St-AAm) aqueous suspension of 0.2 wt% at a temperature of 30, 40, 50, 60, 70, 80 or 90°C and humidity (80%) for 24–72 h. Then, the dry P(St-AAm) PCs films were obtained.

2.4. Characterization

The polydispersity of the latex spheres was detected by a Zeta PALS BI-90plus (Brookhaven Instruments). Transmission electron microscopy (TEM) observations were performed on a H800 transmission microscope (Hitachi, Japan) at an acceleration voltage of 200 kV. To prepare the TEM samples, a small drop of the dispersion of the nano/microspheres was deposited onto a carbon-coated, copper EM grid, and dried at room temperature. Scanning electron microscopy (SEM) images were obtained from a field-emission scanning electron microscope (JEOL JSM-6700, Japan). The reflectance spectra were collected using a fiber-optic spectrophotometer (Ocean Optics, Inc., HR 4000 256 UV-Vis-NIR). All reflectance spectra were measured at the near-normal incidence to the (111) plane of the sample. Water contact angles (CAs) were measured by a Dataphysics OCA20 Contact-Angle System (Germany) at room temperature. The CA values were the averages of five independent measurements. A Nicolet Magna 750 FT-IR spectrometer was used to investigate the chemical surface component of the PCs films by attenuated total reflectance infrared spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Morphology of the As-Prepared PCs Films

Monodisperse latex spheres with a rigid core of PS and an elastomeric shell of PAAm were prepared via emulsion polymerization. The core–shell architecture is confirmed by TEM in Figure 1(a). The image shows that the P(St-AAm) nano/microspheres are quite uniform in size and the core–shell structures are clearly visible. The dark cores represent the PS rich regions, which are surrounded by the lighter shells of the PAAm rich domains. The thin shell of PAAm covers the PS core polymer with acylamino groups anchored upon the surface of latex spheres, which favors the formation of hydrogen bonds among latex spheres. The diameter of P(St-AAm) sphere from TEM image is about 217 nm and the thickness of the PAAm shell is about 25–33 nm.

The PCs films were fabricated by vertical deposition method at a temperature of 30, 40, 50, 60, 70, 80, or 90°C with a relative humidity of 80%, respectively. Figure 1(b) exhibits a typical top-view SEM image of as-prepared PCs assembled from monodisperse P(St-AAm) latex spheres at 60°C . It can be seen clearly that the P(St-AAm) nano/microspheres are in a perfect face-centered cubic (FCC) arrangement over the entire sample with a close-packed plane (111) oriented parallel to the substrate, with each sphere touching six others in one layer.²⁹ From the SEM image, the mean particle size of the P(St-AAm) latex nano/microspheres is about 215 nm, which is in well accordance with that of the result from TEM image. The cross-section SEM image of the PCs film assembled at 60°C

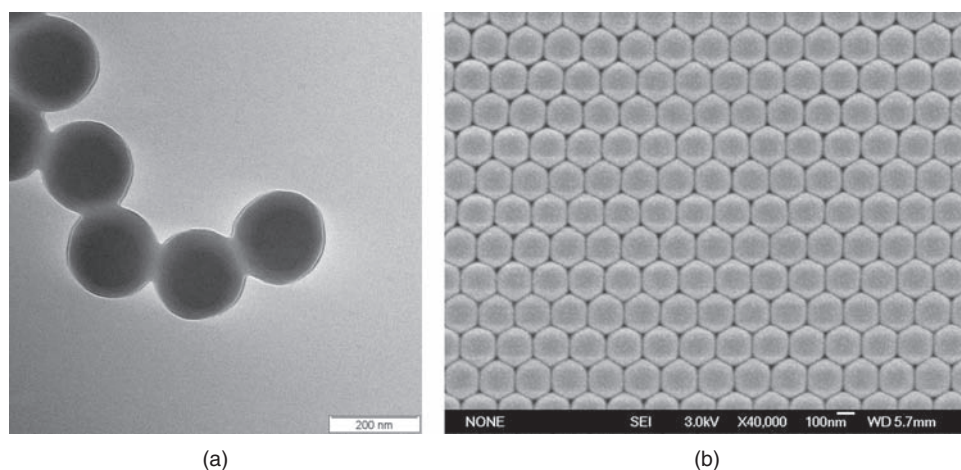


Fig. 1. (a) TEM image of core-shell P(St-AAm) nano/microspheres; (b) The top-view SEM image of as-prepared PCs film assembled at 60 °C.

is shown in Figure 2(a). The thickness of the PCs film is about 5 μm . The image also exhibits that the latex spheres are in contact with the neighboring underlayer. The other top-view SEM images with larger scanning area assembled at different temperatures are shown in Figures 2(b)–(h). From these SEM images, the P(St-AAm) latex nano/microspheres are all arranged orderly and periodically. There is no obvious distinction in morphology among the SEM images of PCs films assembled at different temperatures. It confirms that the assembly temperature has no observable effect on the surface morphology of PCs films.

3.2. Thermoresponsive Wettability

The perfectly packed FCC ordered structure of the PCs film can greatly modify the surface wettability according to the Cassie-Baxter law.^{22,23} Interestingly, the wettability of the PCs films shows a dramatic change when assembled at different temperatures. As shown in Figure 3(a), the water CAs of the films increase with the rise of the assembly temperature. Concretely, at lower temperatures, the water CA is 17.0° (30 °C), 23.7° (40 °C), 34.8° (50 °C), and 39.8° (60 °C). When assembled at higher temperatures, there is a noticeable increase of water CAs, the value reaches 105.5° (70 °C), 116.7° (80 °C), and 127.8° (90 °C). All the photographs of water droplet shape on the PCs films fabricated at different temperatures are shown in Figures 3(b)–(h). Obviously, the hydrophilic PCs film can be obtained at a lower temperature and the hydrophobic PCs film can be fabricated at a higher temperature. It is also observed that the transition temperature of the surface wettability of the as-prepared PCs film is between 60–70 °C. The results indicate that the wettability of the films can be controlled by changing the assembly temperature.

The surface wettability is dependent on surface roughness and chemical composition of the PCs films.^{21,30,31} To elucidate the influence of the surface roughness of the

films on wettability as the temperature varies, the SEM images of the PCs films obtained from different temperatures were observed (shown in Fig. 2). The results exhibit that all the SEM images are exactly similar to each

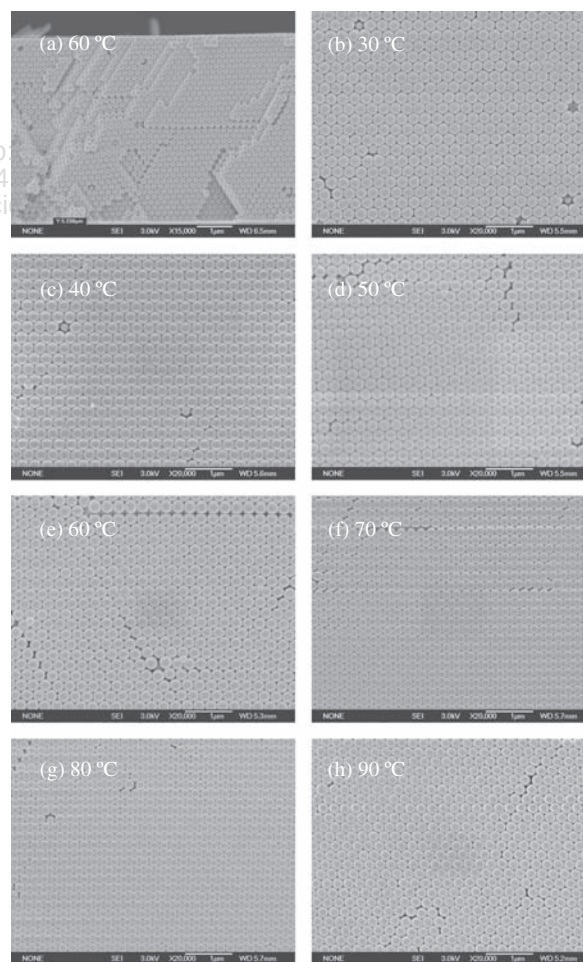


Fig. 2. (a) The cross-section SEM image of the PCs film assembled at 60 °C; (b) to (h) The top-view SEM images of as-prepared PCs films assembled at 30, 40, 50, 60, 70, 80, and 90 °C, respectively.

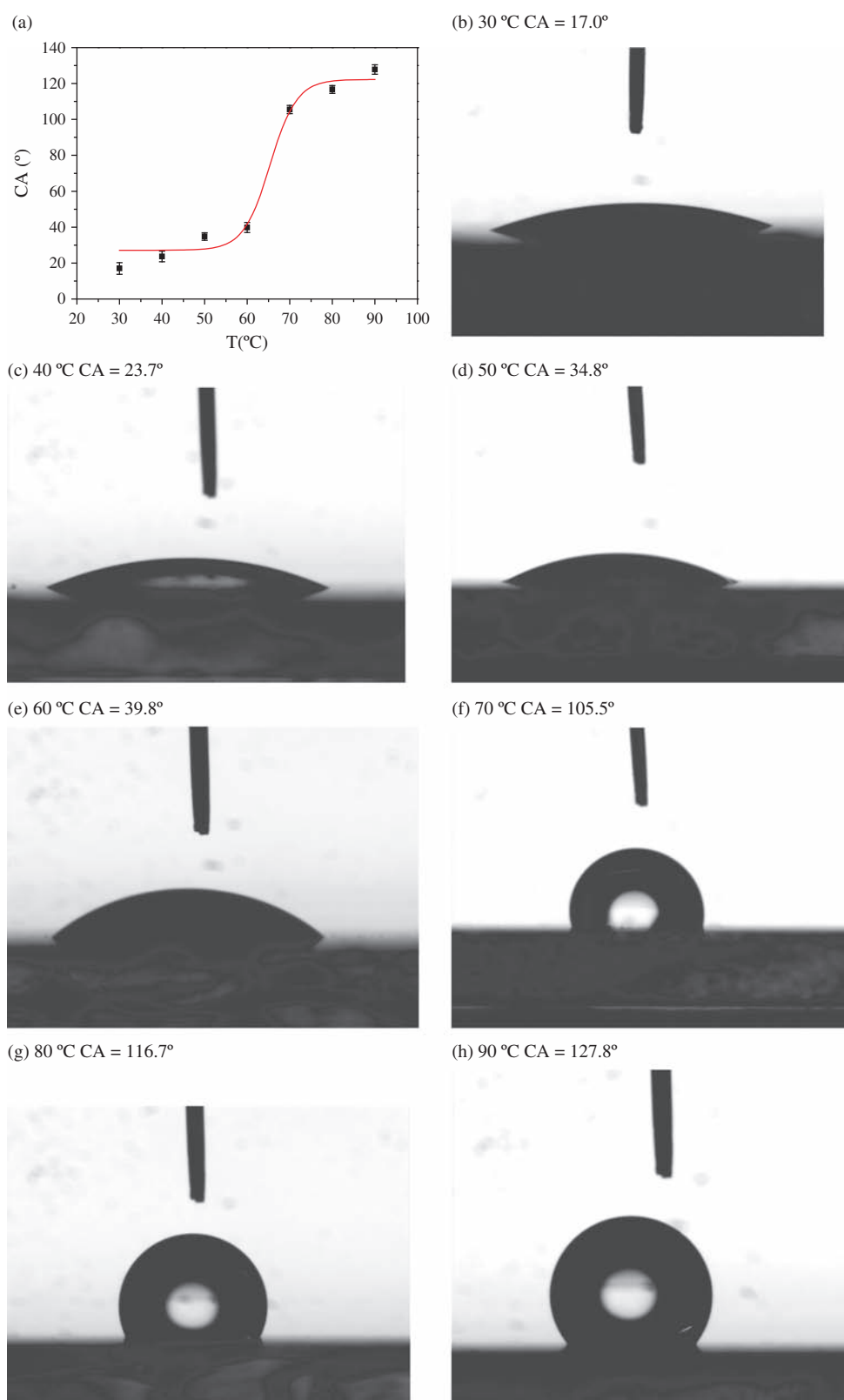


Fig. 3. (a) The relationship of assembly temperature with water CA; (b) to (h) Photographs of water droplet shape on the PCs films assembled at 30 ((b) $\text{CA} = 17.0^{\circ}$), 40 ((c) $\text{CA} = 23.7^{\circ}$), 50 ((d) $\text{CA} = 34.8^{\circ}$), 60 ((e) $\text{CA} = 39.8^{\circ}$), 70 ((f) $\text{CA} = 105.5^{\circ}$), 80 ((g) $\text{CA} = 116.7^{\circ}$) and 90 °C ((h) $\text{CA} = 127.8^{\circ}$), respectively.

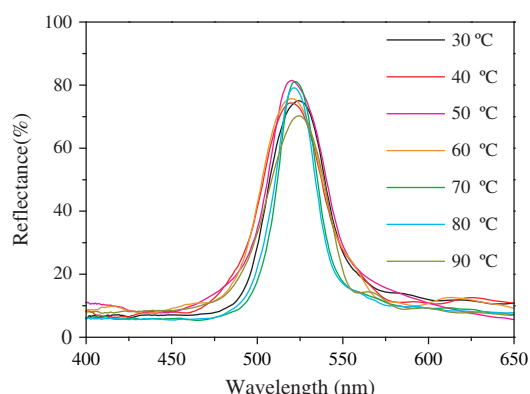


Fig. 4. The reflectance spectra of the PCs films prepared at different temperatures.

other, which demonstrates that there is little morphology change when assembled at different temperatures. Moreover, the reflectance spectra of the films formed at different assembly temperatures were also measured (Fig. 4). The stopband position of the film is 520 nm when prepared at 40, 50, or 60 °C, 521 nm at 70, 80 °C and 524 nm at 30, 90 °C. Obviously, changing the assembly temperature has little effect on the stopband of the films. This indicates that the arrangement of the nano/microspheres does not change clearly at different assembly temperatures. Therefore, the surface roughness of the PCs film has not been affected by the assembly temperatures, which is in agreement with the Refs. [15, 16]. However, the water CAs increase greatly when the assembly temperature is rising (Fig. 3(a)), which indicates that the change of the surface chemical component plays a dominant role in the transition of the wettability behavior of the PCs films.

Attenuated total (internal) reflection Fourier transform IR (ATR-FTIR)^{15,31} was utilized to characterize the surface chemical component of the PCs film prepared at different temperatures, as shown in Figure 5. Herein, the change in the surface chemical component of the PCs film was estimated from the different transmittance intensity

of specific IR bands, in particular, the change in the ratio of transmittance intensity between the hydrophobic and hydrophilic group. In this case, the characteristic transmittance bands of 1668 cm^{-1} (carbonyl group) and 695 cm^{-1} (benzene group) represent the peaks of the hydrophilic and hydrophobic groups, respectively.¹⁵ Figure 5(a) presents the ATR spectra of the PCs films assembled at 30 and 90 °C. The ratio of transmittance intensity between the characteristic bands of 695 and 1668 cm^{-1} is 5.65 when assembled at 30 °C; the ratio rises to 10.76 at 90 °C. This result indicates that the hydrophobicity of the film surface increases with increasing assembly temperature. Similarly, the ratios of transmittance intensity between the characteristic bands of 695 and 1668 cm^{-1} , of the various PCs films assembled from the core-shell P(St-AAm), are plotted as a function of assembly temperature in Figure 5(b). As expected, the ratio of transmittance intensity of the two bands increases with increasing assembly temperature. In addition, there is a rapid increase when assembly temperature is between 60–70 °C, which is in well agreement with the change of the water CAs. The results demonstrate that the surface wettability of the PCs film is dependent on the surface chemical component.

The critical feature of the wettability transition of the PCs film is the change of the surface chemical component of the latex spheres, which arises from reorientation/phase separation of hydrophilic or hydrophobic polymer segments.^{32–34} A possible illustration of the chemical component change of the latex sphere surface during the assembly procedure is shown in Figure 6. The change mainly derives from the phase separation of polymer segments driven toward minimum interfacial energy. Figures 6(a) and (b) present the morphology of two typically stable states of the latex sphere before and after phase separation, respectively. It can be seen from Figure 6(a) that the latex sphere has a hydrophobic PS core and a hydrophilic PAAm shell with acylamino groups anchored on the surface.¹⁶ Thus, the resulting photonic crystal film is hydrophilic when fabricated at a lower temperature.

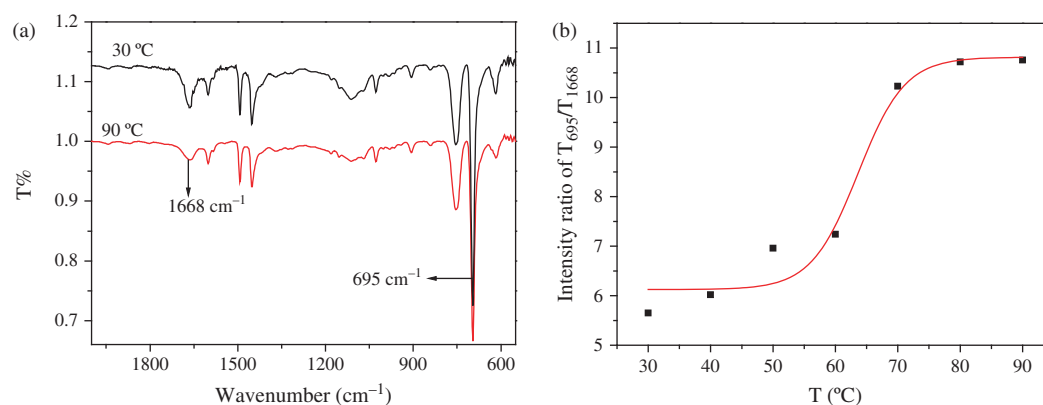


Fig. 5. (a) ATR-FTIR spectra of the PCs films prepared at 30 °C and 90 °C, respectively; (b) The ratio of the transmittance intensity of characteristic bands of 695 and 1668 cm^{-1} at different assembly temperatures.

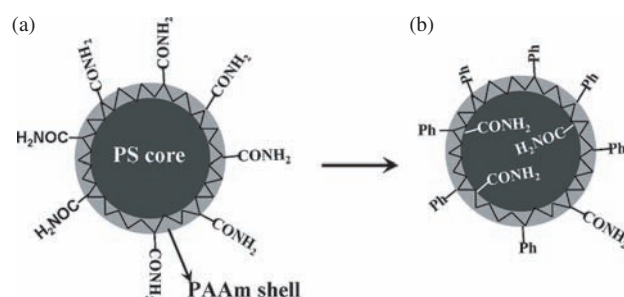


Fig. 6. The schematic illustration of the phase inversion of the latex sphere during the assembly procedure. The conformation mode of the latex sphere before (a) and after (b) phase inversion.

A well-ordered rough surface favors the hydrophilicity of the surface so that the water CA of the film is about 17.0° when assembled at 30°C .^{22,23} With an increase in assembly temperature, thermodynamics drives the polymer chains towards a common minimum energy: the hydrophilic groups tend to shield from the apolar air, and shrink towards the interior of the latex sphere, while hydrophobic CH_2 groups prefer to extend toward the apolar air^{33,34} as the water evaporates during the assembly procedure, as a result, the resulting film is water repellent. This corresponds to a gradual increase of the water CA as the assembly temperature increases. When the assembly temperature further rises, it reaches and overruns a critical value, and most of the polymer segments obtain enough energy for movement. As revealed in Figure 6(b), the hydrophobic CH_2 groups are extended and exposed outside of the latex sphere, and contacted with the apolar air. More importantly, the PS layer migrates to the air surface when the assembly temperature overruns its surface T_g ^{35,36} because of its lower surface energy than PAAm. In contrast, hydrophilic groups are hidden inside of the latex sphere. Consequently, the combination of hydrophobic material and the surface roughness that stems from the periodic structure enhances greatly the water CA^{22,23} and the value reaches to 127.8° for sample prepared at 90°C . Therefore, the PCs films are predominantly hydrophilic at lower temperatures and more hydrophobic at higher temperatures. According to the results of SEM images and the stopband positions of PCs films prepared at different temperatures, the surface roughness for the PCs films has not been changed obviously. As this factor should be constant whatever the assembly temperature, surface chemical composition and surface energy of the assembled latex spheres are more probably responsible for the changes of the final surface wettability of the resulting films.

It is also observed that the PCs film becomes to a hydrophobic surface when the assembly temperature is above 70°C in Figure 3(a). The phenomenon is similar to the result³⁷ that the film is predominantly hydrophilic at lower temperatures and more hydrophobic at higher temperatures. To further understand the reason that the

critical temperature is lower than T_g , the assembly humidity is considered as another important factor to affect the phase inversion. The hydroplastic effect of water on a hydrophilic material can greatly accelerate the extendibility and re-orientation of polymer chains even if it is below its T_g .³⁸ Therefore, the polymer chains of hydrophilic segments from the shell part undergo a great re-orientation at 70°C (far below its T_g of 107.6°C) as a result of the hydroplastic effect of water.

4. CONCLUSIONS

PCs films with tunable wettability and invariable stopband have been fabricated by simply modifying the assembly temperature of an amphiphilic material of P(St-AAm). The tunable wettability is ascribed to phase inversion of the flexible groups of the latex sphere surface during the assembly procedure. The results provide a simple method for fabricating a hydrophobic or hydrophilic PCs film by designing the latex surface appropriately, and the method could be used to control the surface wettability of a wide variety of materials.

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